

# 単層カーボンナノチューブ垂直配向膜の成長過程

## Growth process of vertically aligned single-walled carbon nanotubes

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The growth process of vertically aligned single-walled carbon nanotube (SWNT) films was investigated by means of *in situ* optical analysis and scanning electron microscopy. The measurements reveal that the growth of the SWNT film decreases after longer reaction times. This decrease is attributed to a combination of a diminishing growth rate and burning of the SWNTs due to oxygen in the growth chamber. Using an observed correlation between the optical absorbance of SWNT films and the film thickness, the general behavior of the SWNT film growth process was determined. It was found that burning of the SWNT film could be suppressed by enhancing the quality of the chamber vacuum seal, which also lead to thicker film growth. However, the exponential decrease in catalyst activity has not been circumvented at present. Methods of sustaining the catalyst activity must be developed in order to realize large-scale production of vertically aligned SWNT films.

*Key Words:* Single-walled carbon nanotubes, Alcohol CVD, Vertically aligned, Growth process

### 1. INTRODUCTION

The novel electronic, thermal, and mechanical properties of single-walled carbon nanotubes (SWNTs) have prompted intense studies of these materials. The ability to exploit these unique properties could lead to various new applications. However, producing SWNTs on a large scale with controlled morphologies is a significant hurdle in realizing such applications. The most promising production method to date is catalytic chemical vapor deposition (CVD). An alcohol-based CVD process<sup>(1)</sup> has been developed to produce vertically aligned films of SWNTs several micrometers thick<sup>(2)</sup> on quartz substrates. The present study investigates the growth process of these SWNT films.

### 2. EXPERIMENT

Cobalt catalyst was supported on a quartz substrate by dipping the substrate into a Co-Mo acetate solution (both 0.01 wt% in ethanol), and then withdrawing the substrate from the solution at 4 cm/min<sup>(3)</sup>. The catalyst was oxidized by calcining the dip-coated substrate in air at 400 °C, and then reduced under a flowing Ar/H<sub>2</sub> mixture (3% H<sub>2</sub>) during heating of the CVD chamber. Catalyst prepared by this method resists agglomeration at the growth temperature of 800 °C, resulting in densely deposited (~10<sup>17</sup> m<sup>-2</sup>), mono-dispersed cobalt catalyst particles with diameters of 1-2 nm on a molybdenum oxide layer<sup>(4)</sup>. When the CVD chamber reached the growth temperature of 800 °C, the Ar/H<sub>2</sub> mixture was stopped and ethanol vapor was introduced at a pressure of 10 Torr to initiate SWNT growth. Although it is common practice to add hydrogen as a catalyst activator during the growth stage it was found that SWNTs grown without the addition of hydrogen were better aligned and in higher yield than those grown in the presence of added hydrogen<sup>(5)</sup>.

### 3. RESULTS AND DISCUSSION

Scanning electron microscope (SEM) images from a time-progressive study of the produced SWNT films are shown in Fig. 1. Due to the high catalyst density, bundling of SWNTs occurs early on (Fig. 1(a)), causing vertical alignment of the SWNT film. After 10 min (Fig. 1 (d)) the film thickness exceeds 4

μm, but decreases after longer reaction times. Since the SWNTs are grown at a temperature of 800 °C, and the burning temperature of clean SWNTs in air is 500 - 600 °C<sup>(6,7)</sup>, a likely explanation for the apparent decrease in thickness is burning of the SWNT film by oxygen present in the CVD chamber during growth. If the CVD chamber is not sufficiently sealed, oxygen can enter the chamber and oxidize the catalyst particles (known as catalyst poisoning), as well as burn the SWNT film. It was noted that the decrease in film thickness is suppressed when the CVD chamber seal was sufficient (i.e. the rate of air leaking into the chamber was slow). The presence of hydrogen can help counter this catalyst poisoning by reducing the oxidized catalyst particles<sup>(2)</sup>, but is unnecessary if

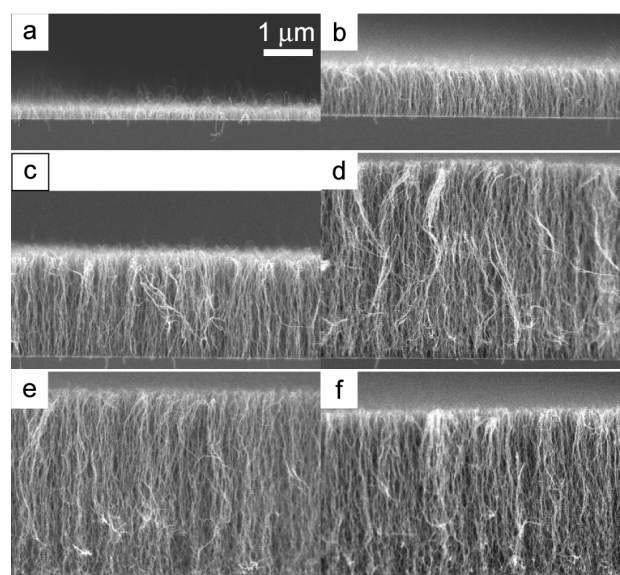


Fig. 1. Growth of aligned SWNT films after (a) 15 seconds, (b) 1 min, (c) 3 min, (d) 10 min, (e) 30 min, and (f) 100 min. The scale bar applies to all images.

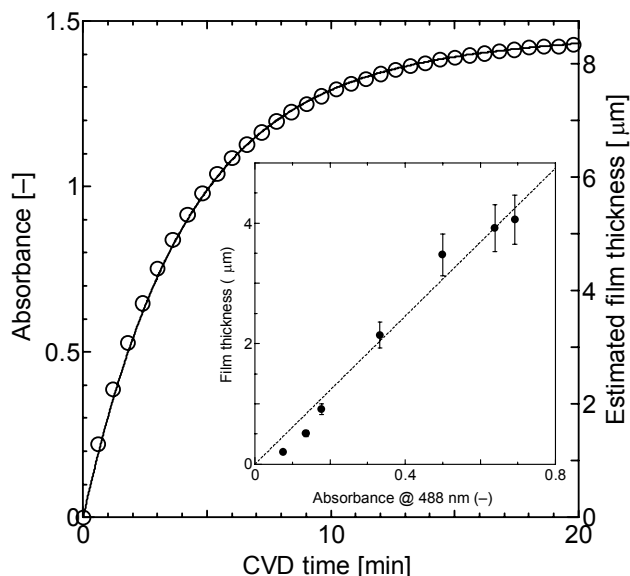


Fig. 2. An *in situ* absorbance trace, from which the SWNT film thickness can be determined based on the thickness-absorbance relationship shown in the inset. The red fitting line shows an exponential decay of the growth rate.

the chamber is sufficiently oxygen-free<sup>(5)</sup>. This illustrates the importance of preserving catalyst activity in SWNT production.

An *in situ* optical measurement technique was developed to further investigate the growth process. Laser light (488 nm) was passed through the quartz substrate inside the furnace during CVD. The intensity of the transmitted light was then measured, from which the time-dependent absorbance at 488 nm was determined, as shown in Fig. 2. The relationship between the film thickness and the measured absorbance is shown in the insert. Using this nearly linear relationship, the SWNT film thickness can be estimated from the absorbance trace, and is indicated on the right axis. Using this technique, we have obtained a time-dependent growth profile of the thickness of the aligned SWNT film. The solid curve is the calculated result according to our deactivating catalyst model, and is an exponential function depending on the initial catalyst activity and the time constant of the active catalyst<sup>(8)</sup>. In brief, we simply assume that the growth rate  $\eta = dM/dt$  [mol m<sup>-2</sup> s<sup>-1</sup>], decays in time due to catalyst poisoning with a decay time constant  $\tau$  [s] such that

$$\frac{d\eta}{dt} = -\frac{1}{\tau}\eta. \quad (1)$$

The number of moles of carbon formed into SWNTs per area,  $M(t)$  [mol m<sup>-2</sup>], then becomes

$$M(t) = \eta_0\tau\left(1 - e^{-t/\tau}\right), \quad (2)$$

where  $\eta_0$  is the initial growth rate, at  $t=0$ . The absorbance  $A(t)$  is  $M(t)$  multiplied by the molar absorption cross section of the aligned SWNT sample,  $\varepsilon$  [m<sup>2</sup> mol<sup>-1</sup>], evaluated at  $t = \infty$ ,

$$A(t) = \varepsilon_\infty M(t) = \varepsilon_\infty\eta_0\tau\left(1 - e^{-t/\tau}\right). \quad (3)$$

For the curve in Fig. 2,  $\varepsilon_0 = 28.0$  m<sup>2</sup> mol<sup>-1</sup>,  $\eta_0 = 2.08 \times 10^{-4}$  mol m<sup>-2</sup> s<sup>-1</sup>, and  $\tau = 245$  s. It is clear that the growth rate of the SWNT film exponentially decreases with decreasing catalyst activity.

Employing the *in situ* measurement technique described above, evidence of burning and the effect of the CVD environment on the SWNT film was observed directly, as shown in Fig. 3. The quality of the vacuum chamber seal was evaluated by evacuating the CVD chamber to a pressure of 2 Pa, sealing the chamber by closing all valves to the vacuum pump, and then measuring the time required for the chamber pressure to rise from

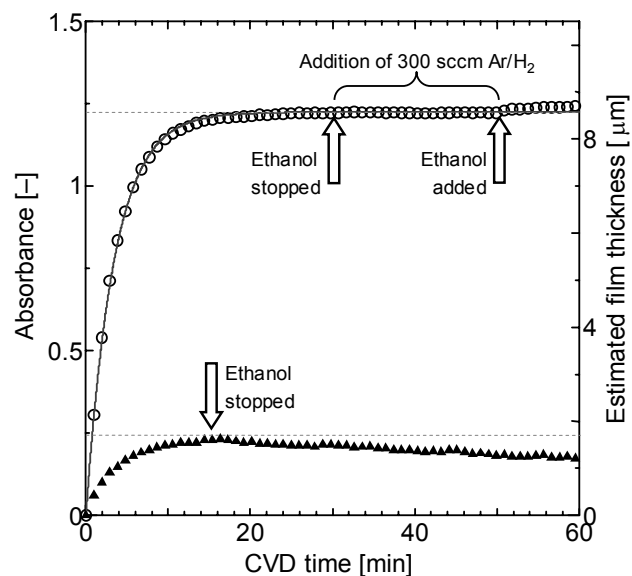


Fig. 3. Absorbance traces showing burning of the SWNT film when the leak rate is fast (filled triangles), and no burning when slow (open circles).

2 to 5 Pa (referred to as the “leak time”). After determining the leak time, the chamber was heated to the growth temperature of 800 °C, and a SWNT film was grown according to the procedure described in the experimental section. In the case of the sample indicated by the filled triangles in Fig. 3, the leak time was 7 min. This sample was grown for 15 min, at which time the ethanol supply was cut-off (indicated in the figure by an arrow), and the CVD chamber was held at 800 °C for an additional 45 min. An appreciable decrease in film thickness due to burning of the film by oxygen in the CVD chamber was observed. A dashed horizontal line at the maximum height is shown for reference. For a second sample, indicated by open circles in Fig. 3, the leak time was 23 min. This indicates less oxygen in the CVD chamber due to a significantly better vacuum seal. It was soon obvious that the aligned SWNT film grown under this condition was much thicker than in the former case, which is attributed to the higher initial catalyst activity due to the cleaner (oxygen-free) growth environment. In the second case, the ethanol supply was stopped after 30 min of growth. The chamber was then held for 10 min at 800 °C. After 10 min, no decrease in film thickness was observed, compared to a noticeable decrease after the same time in the previous experiment (filled triangles). After 10 min had expired, 300 sccm Ar/H<sub>2</sub> (3% H<sub>2</sub>) was flowed through the CVD chamber for an additional 10 minutes. Recall this is the same mixture present during the heat-up stage prior to SWNT growth in order to activate the catalyst particles by reduction. After introducing the Ar/H<sub>2</sub> mixture for 10 min the Ar/H<sub>2</sub> flow was stopped, and ethanol was again introduced into the chamber at the normal growth pressure of 10 Torr. After reintroduction of ethanol, a slight increase in absorbance (film thickness) was observed, indicating additional growth from reactivated catalyst. However, the retrieved catalyst activity was quite low, thus a more firmly established method for catalyst reactivation should be sought in future studies.

## 5. REFERENCES

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